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(54) **RUBBER COMPOSITION AND METHOD OF  
MANUFACTURING RUBBER GOODS USING THE  
SAME**

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a rubber composition and a rubber goods using the same which increases a curing speed without deteriorating processability.

SOLUTION: The rubber composition contains a

microcapsule which is coated with a radically degradable resin and has a curing agent or a curing accelerator as a core. The free radical-degradable resin is desirably a resin having a secondary or higher carbon atom in the main chain. A method of manufacturing rubber goods comprizing a process of kneading the rubber composition, a process of irradiating the rubber composition thus kneaded with an electron beam and a process of curing thereafter is also provided.

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CLAIMS

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[Claim(s)]

[Claim 1] The rubber constituent containing the microcapsule which made the vulcanizing agent and/or the vulcanization accelerator the heart agent, and was covered with the radical decay type resin.

[Claim 2] A radical decay type resin is a rubber constituent according to claim 1 which is the resin which has the carbon atom of the second more than class in a principal chain.

[Claim 3] The process which kneads the rubber constituent of a claim 1, the process which irradiates an electron ray at the rubber constituent kneaded and obtained, the manufacture method of rubber goods which consists of the process which carries out after cure.

[Claim 4] Rubber goods are the manufacture methods according to claim 3 which are a tire.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of of the rubber constituent for tires and tire which made vulcanization speed quick, without falling the manufacture method of the rubber goods which used the rubber constituent and this rubber constituent, especially processability.

[0002]

[Description of the Prior Art] In order to shorten the curing time of a rubber constituent conventionally, blending a vulcanization accelerator with a quick vulcanization speed was performed. This vulcanization accelerator had the problem which starts vulcanization partially and produces rubber burning in the processing process before vulcanization. Then, by blending the microcapsule which covered the vulcanizing agent or the vulcanization accelerator with thermoplastics etc., thermoplastics is dissolved at the heating temperature at the time of vulcanization, and the technology of emitting a vulcanizing agent and a vulcanization accelerator and making vulcanization starting is proposed (JP,48-25042,A, JP,10-17706,A, JP,10-17707,A).

[0003] the method of dissolving the thermoplastics which is covering material of a microcapsule at the heating temperature at the time of the vulcanization in the conventional technology, emitting a vulcanizing agent and a vulcanization accelerator, and making vulcanization starting -- if -- the time for the time, vulcanizing agent, and vulcanization accelerator for covering material dissolving being spread is taken, and it cannot be said as a means effective for shortening of a curing time. Furthermore, there was a problem that uniform distribution with the rubber constituent of a vulcanizing agent and a vulcanization accelerator could not be attained. Therefore, although vulcanization took place enough around the microcapsule of a rubber constituent, the problem that crosslinking density fell had arisen in the field distant from the microcapsule.

[0004]

[Problem(s) to be Solved by the Invention] If it is equalization, this invention solves the above-mentioned problem, makes vulcanization speed quick, without falling processability, moreover closes distribution in the rubber constituent of a vulcanizing agent and a vulcanization accelerator, and offers the manufacture method of rubber goods using the rubber constituent and this rubber constituent which have improved basic properties, such as intensity of rubber goods, and a pace of expansion.

[0005]

[Means for Solving the Problem] this invention is a rubber constituent containing the microcapsule which made the vulcanizing agent and/or the vulcanization accelerator the heart agent, and was covered with the radical decay type resin. A radical decay type resin is a resin which has the carbon atom of the second more than class in a principal chain preferably here.

[0006] Other invention is the manufacture methods of the process which kneads the rubber constituent containing the microcapsule which made the vulcanizing agent and/or the vulcanization accelerator the heart agent, and was covered with the radical decay type resin, the process which irradiates an electron ray at the rubber constituent kneaded and obtained, and the rubber goods which consist of the process which carries out after cure. A tire is preferably applied as rubber goods here.

[0007]

[Embodiments of the Invention] Especially a limit does not have the rubber component used for the rubber constituent of this invention, and various rubber can be used for it. for example, the rubber component which contains either at least among natural rubber (NR) or diene system synthetic rubber -- it can be used -- as diene system synthetic rubber -- a styrene butadiene rubber (SBR), (polybutadiene-rubber BR) (polyisoprene-rubber IR) ethylene-propylene-diene rubber (EPDM), chloroprene rubber (CR), acrylonitrile-butadiene rubber (NBR), isobutylene isoprene rubber (IIR), etc. -- the inside of a rubber component -- one kind -- or two or more kinds may be included With in addition, ethylene-propylene-diene rubber (EPDM) It is what contains the third diene component in ethylene-propylene rubber (EPM). here with the third diene component It is nonconjugated diene of carbon numbers 5-20. For example, 1, 4-pentadiene, 1, 4-hexadiene, 1, 5-hexadiene, 2, 5-dimethyl - 1, 5-hexadiene and 1, and 4-OKUTA diene, For example, annular dienes, such as 1, 4-cyclohexadiene, cyclo-octadiene, and a dicyclopentadiene, For example, 5-ethylidene-2-norbornene, 5-butyldiene-2-norbornene, Alkenyl norbornene, such as 2-metallyl-5-norbornene and 2-isopropenyl-5-norbornene, etc. is mentioned, and a dicyclopentadiene, 5-ethylidene-2-norbornene, etc. can especially be used in a diene.

[0008] This core material is covered with the radical decay type resin for the microcapsule blended with the rubber constituent of this invention, using a vulcanizing agent or a vulcanization accelerator as a core material.

[0009] As a vulcanizing agent, organic peroxide or a sulfur system vulcanizing agent can be used. As organic peroxide, for example Benzoyl peroxide, dicumyl peroxide, G t-butyl peroxide, t-butyl cumyl peroxide, Methyl ethyl ketone peroxide, a cumene hydroperoxide, 2, the 5-dimethyl -2, 5-di-tert-butyl peroxide hexane, 2, the 5-dimethyl -2, 5-JI (benzoylperoxy) hexane, 2, the 5-dimethyl -2, 5-di-tert-butyl peroxide hexyne -3 or 1, 3-screw (t-butyl par OKISHIPUROPURU) benzene, G tert-butyl peroxide-diisopropylbenzene, t-butyl par oxybenzene, 2, 4-dichlorobenzoyl peroxide, 1, and 1-G tert-butyl peroxide - 3, 3, a 5-trimethyl siloxane, n-butyl -4, a 4-G t-butyl par OKISHIBARE rate, etc. can be used. In these, dicumyl peroxide, t-butyl par oxybenzene, and G tert-butyl peroxide-diisopropylbenzene are desirable. Moreover, as a sulfur system vulcanizing agent, sulfur, morpholine disulfide, etc. can be used, for example. Sulfur is desirable as a vulcanizing agent.

[0010] It is desirable to the rubber component 100 weight section the 0.3 - 5.0 weight section and that 1.0-2.5 weight section combination especially of the vulcanizing agent is carried out.

[0011] It is possible to use a sulfenamide system, a thiazole system, a thiuram system, a thiourea system, a guanidine system, a dithiocarbamic-acid system, an aldehyde-amine system or an aldehyde-ammonia system, an imidazoline system, or the thing containing at least one of xanthate system vulcanization accelerators as a vulcanization accelerator.

[0012] As a sulfenamide system, sulfenamide system compounds, such as CBS (N-cyclohexyl-2-benzo thiazyl sulfenamide), TBBS (N-t-butyl-2-benzo thiazyl sulfenamide), N, and N-dicyclohexyl-2-benzo thiazyl sulfenamide, N-oxy-diethylene-2-benzo thiazyl sulfenamide, N, and N-diisopropyl-2-benzothiazole sulfenamide, etc. can be used, for example.

[0013] As a thiazole system, thiazole system compounds, such as MBT (benzo thiazyl disulfide), MBTS (dibenzothiazyl disulfide), 2-(2, 4-dinitrophenyl) mercaptobenzothiazole, and 2-(2, 6-diethyl-4-morpholino thio) benzothiazole, etc. can be used, for example.

[0014] As a thiuram system, thiuram system compounds, such as TMTD (tetramethylthiuramdisulfide), a tetraethylthiuram disulfide, tetramethylthiurammonosulfide, JIPENTA methylene thiuram disulfide, JIPENTA methylene thiuram monosulfide, dipentamethylenethiuramtetrasulfide, a JIPENTAMECHIREN thiuram hexa sulfide, tetrabutylthiuram disulfide, and pentamethylene thiuram tetrasulfide, can be used, for example.

[0015] As a thiourea system, thiourea compounds, such as a thia carbamide, diethyl thiourea, a dibutylthiourea, trimethyl thiourea, and JIORUTO tolyl thiourea, etc. can be used, for example.

[0016] As a guanidine system, guanidine system compounds, such as a diphenylguanidine, JIORUTO tolyl guanidine, a triphenyl guanidine, an ortho tolyl biguanide, and diphenylguanidine phthalate, can be used, for example.

[0017] As a dithiocarbamic-acid system, for example Ethyl phenyl dithiocarbamic-acid zinc, Butylphenyl dithiocarbamic-acid zinc, a sodium dimethyldithiocarbamate, A zinc dimethyldithiocarbamate, a zinc diethyldithiocarbamate, Zinc dibutyldithiocarbamate, JIAMIRU

dithiocarbamic-acid zinc, The complex salt of dipropyl dithiocarbamic-acid zinc, pentamethylene dithiocarbamic-acid zinc, and a piperidine, Hexadecyl (or octadecyl) isopropyl dithiocarbamic-acid zinc, Dibenzyl dithiocarbamic-acid zinc, a sodium diethyldithiocarbamate, Dithiocarbamic-acid system compounds, such as a pentamethylene dithiocarbamic-acid piperidine, a dimethyl dithiocarbamic-acid selenium, a diethyldithiocarbamic-acid tellurium, and JIAMIUR dithiocarbamic-acid cadmium, etc. can be used.

[0018] As an aldehyde-amine system or an aldehyde-ammonia system, an aldehyde-amine system or aldehyde-ammonia system compounds, such as an acetaldehyde-aniline reactant, a butyraldehyde-aniline condensate, a hexamethylenetetramine, and an acetaldehyde-ammonia reactant, etc. can be used, for example.

[0019] As an imidazoline system, imidazoline system compounds, such as 2-mercapto imidazoline, etc. can be used, for example. As a xanthate system, xanthate system compounds, such as dibutyl xanthogenic-acid zinc, etc. can be used, for example.

[0020] the loadings of the vulcanization accelerator in a rubber constituent -- the rubber component 100 weight section -- receiving -- 0.5 - 6 weight section -- it is the range of the 1.0 - 3.0 weight section preferably and the case where sulfur is used for a vulcanizing agent -- sulfur (S) and a vulcanization accelerator (A) -- comparatively (S/A) -- 0.1-3.0 -- it is the range of 0.6-1.5 preferably. By making the rate of sulfur and a vulcanization accelerator into the above-mentioned range, monosulfide bridge formation can be formed effectively and the thermal resistance of a vulcanized-rubber constituent and fatigue resistance can be improved.

[0021] In this invention, a radical decay type resin is used for the film material of a microcapsule. A radical decay type resin means what has the carbon atom of the second more than class in the molecule principal chain of a resin here. That is, it is the resin which has substituents other than the hydrogen more than a piece in the carbon atom of the molecule principal chain of a resin. The carbon which a substituent combines generates a radical easily and a substituent says what induces decomposition of a pitch child's principal chain here, when an electron ray is irradiated with alkyl groups, such as a methyl group, an ethyl group, and a propyl group, an aromatic machine, a halogen, etc.

[0022] The resin which has the above-mentioned substituent with polystyrene, polyethylene, polypropylene, polyurethane, a Nylon, acrylic resin, methacrylic resin, an ethylene-acrylic copolymer, an ethylene vinylacetate copolymer, vinyl chloride resin, butadiene resins, a butene resin, a polycarbonate, ABS plastics, an AS resin, a polyacetal, polyester, etc. can be used for a radical decay type resin.

[0023] As for the aforementioned radical decay type resin, what has 100-200 degrees C of 60-250 degrees C of the softening temperature in a 120-160-degree C temperature requirement especially preferably is desirable. A microcapsule may break in the case of kneading [ degrees C / 60 ] of softening temperature of a low and a rubber constituent. When softening temperature exceeds 250 degrees C and decomposition of the film agent of the microcapsule by electron beam irradiation is inadequate on the other hand, in the usual curing temperature of a rubber constituent, this film material resin does not dissolve and a vulcanizing agent and a vulcanization accelerator are not emitted from a microcapsule. Therefore, as for the kind of film material resin, being selected by the relation with a curing temperature is desirable.

[0024] The technique of microencapsulation generally known is adopted as a method of covering a vulcanizing agent and a vulcanization accelerator with a radical decay type resin, and manufacturing a microcapsule. Suitably, it considers as the medium of encapsulation of the inside of liquid drying, i.e., underwater and an oil, and the method of distributing the film material matter solution containing the heart matter guttate, flying a solvent, and forming a hard capsule film into it, is adopted. By this method, first, the boiling point is lower than that of water, vapor pressure is large, the solvent with which it moreover does not mix with water is chosen, and wallplate polymer is melted in this solvent. The solution used as the heart matter is distributed in this solution, and the emulsification object of type (W/O) is built.

[0025] The solution which contains protective colloid as an encapsulation medium independently is prepared, and a previous emulsification object is put in, it distributes, stirring this, and a [(W/O)/W] type compound emulsion is made. As for this system, \*\*\*\* of the form where the aqueous drop was

surrounded with the polymer solution is floating underwater. If warming, reduced pressure, a solvent extraction, etc. are operated in this system and it is made to dry the solvent of polymer, the hard film of polymer will be formed and a microcapsule will be made.

[0026] Moreover, in the suspension method in mind which can be adopted as other methods, the heart matter (powder) is made to fluidize and suspend by the air current, and it sprays as a milky lotion which made the suspension particle front face emulsify the film material of thermoplastics. And slurring air can be heated, a solvent can be evaporated and a capsule film can be made to form. Moreover, the milky lotion which made the film material of a resin emulsify is made to suspend a core material, and the suspension can be sprayed and atomized, it can be made to be able to dry momentarily, and an encapsulation film can be made to form by the spray drying method. The method (how to encapsulate [ gives a shock with a centrifugal force etc., and ] it on the surface of a core material, after mixing a core material particle and a film material particle finer than it, as embeds a film agent) of furthermore encapsulating fine particles by dry type etc. can be adopted, and especially the manufacture method of a microcapsule is not limited.

[0027] As for the microcapsule obtained by the above-mentioned method, it is desirable that both sum total contains a vulcanizing agent or a vulcanization accelerator 30 to 95% of the weight when using simultaneously 30 - 95 % of the weight and a vulcanizing agent, or a vulcanization accelerator as a core material, respectively. It is 40 - 80 % of the weight preferably. Less than 30% of the weight of a case, disassembly of the covering material resin at the time of electron beam irradiation or dissolution of the covering material resin at the time of vulcanization is inadequate, and it becomes inadequate discharge of a vulcanizing agent and a vulcanization accelerator and distributing. On the other hand, if it exceeds 95 % of the weight, manufacture of a uniform microcapsule will become difficult.

[0028] Various bulking agents and an additive can be used in the rubber constituent of this invention. For example, carbon black can be blended to the rubber component 100 weight section as a bulking agent, and the loadings are usually the 10 - 120 weight section. As a kind of carbon black, FEF, skin reactive factor, HAF, ISAF, SAF, etc. can be used.

[0029] Moreover, it is possible to use an amine system, a phenol system, an imidazole system, a carbamic-acid metal salt, a wax, etc. as an antioxidant (degradation inhibitor), choosing them suitably.

[0030] Furthermore, in the rubber constituent of this invention, in order to scour and to raise processability, a softener can also be used together. As a softener, wax; linolic acid, such as fatty-oil system softener; tall oil; sub; beeswax, such as petroleum system softener; castor oil, such as a process oil, a lubricating oil, paraffin, a liquid paraffin, petroleum asphalt, and vaseline, linseed oil, rapeseed oil, and palm oil, a cull navarho, and lanolin, a palmitic acid, stearin acid, a lauric acid, etc. are mentioned.

[0031] Furthermore by this invention, a plasticizer, for example, DMP (dimethyl phthalate), DEP (diethyl phthalate), DBP (dibutyl phthalate), DHP (diheptyl phthalate), and DOP (dioctyl phthalate), DINP (phthalic acid diisononyl ester), DIDP (diisodecyl phthalate), BBP (phthalic acid benzyl butyl ester) and DLP (dilauryl phthalate), DCHP (dicyclohexyl phthalate), tetrahydrophthalic anhydride ester, etc. can be blended if needed.

[0032] moreover, as a white bulking agent, a silica, clay, an alumina, talc, a calcium carbonate, a magnesium carbonate, an aluminum hydroxide, a magnesium hydroxide, a magnesium oxide, titanium oxide, etc. can be used, and these are independent -- or two or more sorts can be mixed and it can use A silica, clay, an aluminum hydroxide, and an alumina are especially desirable.

[0033] Moreover, when blending a white bulking agent with a rubber constituent, it is desirable to make a coupling agent contain. As a coupling agent, an aluminum NETO system coupling agent, a silane system coupling agent, a titanium system coupling agent, etc. can be used.

[0034] For manufacturing rubber goods, it carries out by the following method using the rubber constituent of this invention. With the microcapsule which contains sulfur or a vulcanization accelerator in a rubber component, the additive of bulking agents, such as carbon black, and a plasticizer, and others is blended, and it kneads by Banbury or the kneader. And when using the rubber constituent which kneaded for a tire composition member, thickness forms in the sheet of the range which is 0.3-5mm with a roll etc. If dimensional stability [ aptitude / a tire composition

member.] is not obtained but it exceeds 5mm on the other hand when the thickness of a sheet is less than 0.3mm, an electron ray will not penetrate to the interior of a rubber sheet. Therefore, decomposing [ of the covering material resin of a microcapsule ] becomes inadequate by electron beam irradiation, it will wait for dissolution of the covering material resin by the temperature up in a vulcanization process, vulcanization will start, and it is a book. The range of the thickness of a sheet is 0.5-1.2mm preferably.

[0035] In this invention, in order to irradiate an electron ray at the sheet of a rubber constituent, the electron-beam-irradiation equipment generally used in the tire industry can be used. And the acceleration voltage of electron beam irradiation is usually the range of 0.1MeV-5MeV, and 40 or less Mrads of quantity of radiation are the range of 3 - 20Mrad preferably. The covering material resin of a microcapsule carries out synchronization also of the bridge formation between rubber molecule principal chains with decomposition of decay, i.e., a rubber molecule principal chain, by electron beam irradiation. Therefore, it becomes possible to make decay of the covering material resin of a microcapsule give priority to and cause by adjusting the amount of electron beam irradiation.

[0036] The laminating of the sheet of the rubber constituent which carried out the above-mentioned electron beam irradiation is carried out to other sheets as a simple substance, or it is fabricated in a predetermined configuration, and is set at the usual vulcanization process. Vulcanization is performed by the use of a product with a press or metal mold. Vulcanization is usually performed for 5 - 60 minutes at 130-180 degrees C.

[0037] this invention can be applied to various rubber goods, and the kind of rubber goods selects arbitrarily combination, the sheet thickness and configuration, and also electron-beam-irradiation conditions of a rubber constituent. this invention constitutes a rubber constituent in predetermined thickness, irradiates an electron ray at this, and can apply this to a laminating or the rubber goods which can be fabricated. for example, the composition of a tire -- the tread section which is a member, the sidewall section, a carcass ply, a belt ply, a bead filler, etc. can be adopted still more suitable for an offset blanket, an imprint roller, etc. In addition, the rubber constituent of the shape of an aforementioned sheet may be the composite under which a reinforcement code, for example, a steel code, the polyester code, the nylon code, the Kevlar code, and the rayon code were laid by predetermined density. laminate molding after the composition member of these tires irradiates an electron ray -- carrying out -- metal mold -- a tire can be manufactured by vulcanizing inside

[0038]

[Example] (1) Dissolve manufacture polystyrene (softening temperature of 100 degrees C) 7.5g of a microcapsule in dichloromethane 150ml, and add and stir 15g of sulfur in this solution. A little surfactant is added at this time. Next, the solution containing the above-mentioned sulfur is dropped at PVA solution (what dissolved PVA12g in 1200 cc of water). Stirring was continued after that for 1 hour, it filtered and dried and the microcapsule was obtained. The microcapsule contains sulfur 43.5% of the weight.

[0039] (2) Using the microcapsule produced by the method of production of a rubber constituent, and the electron-beam-irradiation above (1), it kneaded by combination of Table 1 and the rubber constituent of the shape of a sheet with a thickness of 1mm was manufactured. the conditions which show acceleration voltage to this rubber sheet by 1MeV in Table 1 -- after changing the exposure like and irradiating an electron ray, while carrying out the KYURASUTO examination, the rubber sheet which carried out electron beam irradiation was vulcanized for 20 minutes at 150 degrees C, and the physical-properties evaluation was carried out The result is shown in Table 2.

[0040]

[Table 1]

配合剤	実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
ポリイソプレン(IR)	100	100	100	100	100
カーボンブラック	50	50	50	50	50
アロマイル	10	10	10	10	10
ステアリン酸	2	2	2	2	2
酸化亜鉛	2.5	2.5	2.5	2.5	2.5
硫黄	-	-	-	-	1
加硫促進剤	2	2	2	2	2
マイクロカプセル	3.4	3.4	3.4	3.4	-
(硫黄換算)	(1.5)	(1.5)	(1.5)	(1.5)	-
電子線照射量	6Mrad	18Mrad	36Mrad	未照射	未照射

使用した薬品

(注 1) IR:JSR 社製の IR2200

(注 2) カーボンブラック:三菱化学(株)製のダイヤブラックH

(注 3) アロマイル:(株)ジャパンエナジー製の JOMO X140

(注 4) ステアリン酸:日本油脂(株)製

(注 5) 酸化亜鉛:三井金属鉱業(株)製の酸化亜鉛 2 種

(注 6) 硫黄:鶴見化学(株)製の粉末硫黄

(注 7) 加硫促進剤:大内新興化学工業(株)製のノクター NS

(N-tert-ブチル-2-ベンゾチオチオキサントニウム)

(注 8) マイクロカプセル化硫黄:実施例で記載した方法で製造した。

ステレン/硫黄=1/2(重量比)

[0041]

[Table 2]

		実施例			比較例	
		1	2	3	1	2
キ ュ ラ ス ト 試 験	130℃					
	ML (kgf · m)	2.3	2.4	2.5	2.2	2.3
	Tc10 (分)	17.2	11.1	4.5	25.2	24.9
	Tc90 (分)	31.0	30.0	25.1	37.1	34.9
	150℃					
	Tc10 (分)	4.7	3.3	2.0	6.6	6.4
	Tc90 (分)	7.9	7.6	5.9	9.6	9.2
	M100 (Mpa)	1.91	1.86	1.85	1.99	2.01
	M300 (Mpa)	12.1	12.2	12.0	10.9	11.0
加 硫 ゴ ム 物 性	伸張強度 Tb (Mpa)	27.5	26.5	24.6	27.8	27.6
	破断時伸び Eb (Mpa)	500	480	450	500	500
	硬さ Hs (JIS A)	58	58	56	63	63

[0042] (3) Test method JIS <a KYURASUTO examination> According to K6300, ML (minimum value of torque), Tc (10), and Tc (90) were measured using the oscillating-type vulcanization testing machine (curelast meter).

[0043] <Tension test> JIS According to K6251, elongation was measured by speed-of-testing 500 mm/min using the dumbbell-like No. 3 system test piece at the time of tensile strength and fracture.

[0044] <Hardness (Hs)> JIS According to K6253, it measured with the durometer of Type A.

[0045] (4) The evaluation result of an evaluation result example and the example of comparison is shown in Table 2. Although an example 1 and an example 2 carry out electron beam irradiation of the sheet of the rubber constituent which blended the sulphuric microcapsule, there are 10 minutes or more of 130 degrees C [ which is the index of scorch time ] Tc (10), and scorch time is secured enough. Furthermore, it was able to be extended at the time of tensile strength (Tb) and fracture, and (Eb) was hardly able to be affected, but the modulus (M100) and the degree of hardness were able to



be lowered 100%, and the modulus (M300) was able to be raised 300% conversely. When it is used as a rubber constituent for tires, since crookedness fatigue nature and abrasion resistance are improved, these properties are advantageous. In addition, since the inclination for vulcanized-rubber physical properties to also fall will be accepted while scorch time becomes short, and vulcanization advances at the time of electron beam irradiation if the electron ray of 20 or more Mrads is irradiated like an example 3, if the amount of electron beam irradiation is raised to 40 or more Mrads, it will become disadvantageous. For the reason, by 20 or less Mrads and combination which means shortening of a curing time, an exposure is suitably chosen by 40 or less Mrads at combination of physical-properties serious consideration.

[0046] In addition, it should be thought that the form and example of operation which were indicated this time are [ no ] instantiation at points, and restrictive. The range of this invention is shown by the above-mentioned not explanation but claim, and it is meant that a claim, an equal meaning, and all change in within the limits are included.

[0047]

[Effect of the Invention] A curing time can be shortened being able to irradiate an electron ray at the arbitrary time of the process before vulcanization, being able to make a vulcanizing agent and a vulcanization accelerator emit from a microcapsule, and adjusting scorch time effectively, since the vulcanizing agent or the vulcanization accelerator was blended with the rubber constituent by this invention like \*\*\*\* as a microcapsule which the radical decay type resin covered. A modulus and a degree of hardness can be lowered 100 more%, and a modulus can be raised 300% conversely. When the rubber constituent to apply is applied to the composition member of a tire, the crookedness fatigue nature of a tire and abrasion resistance improve.

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[Translation done.]